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Mn-Ta-OXIDES: PHASE RELATIONSHIPS AT 1200°C

by

A. C. Turnock

Paper prepared for submission for publication
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August 10, 1965

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c.c. Dr. Bright
Physical Chemistry Section
MSD files

Mineral Sciences Division
A. T. Prince, Chief

555 Booth Street,
Ottawa 4, Ontario.
November 19, 1965.

Dr. Allan C. Turnock,
Department of Geology,
University of Manitoba,
Winnipeg, Manitoba.

Dear Allan:

As I forecast a few days ago, your Mn-Ta-O paper has now come back from the printers and I am enclosing 6 copies, three for you to retain yourself and three to enable you to satisfy the requirements of the Editor of the Journal of the American Ceramic Society (Mr. Frank P. Reid, 4055 North High Street, Columbus, Ohio 43214, U.S.A.).

Insofar as the figure on page 3 is concerned, the Journal requires a glossy print. I am therefore, also enclosing two small and one large glossy prints of this figure. I suggest you send all three to the Journal and let them take their pick.

Incidentally, the Director has given his approval to the publication of this paper and you may inform the Editor of the Journal that the Department of Mines and Technical Surveys, Government of Canada, will be prepared to assume any page charges.

I would, incidentally, like to be assured of the safe arrival on your desk of this paper. It would be a good idea to register the package that you send to the Editor of the Journal.

Here's wishing you all the best -

Yours very sincerely,

Norman F.H. Bright,
Head,
Physical Chemistry Section.

Encls.

MINES BRANCH

Mineral Sciences Division

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(Author) A. C. Turnock

(Date) August 10, 1965

Internal Investigation Report No. MS-65-106

TITLE: Mn-Ta-Oxides: Phase Relationships at 1200°C

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Mineral Sciences Division Internal Report MS-65-106

Mn-Ta-OXIDES: PHASE RELATIONSHIPS AT 1200°C

by

A. C. Turnock*

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ABSTRACT

Subsolidus phase relationships among oxides in the system Mn-Ta-O have been experimentally determined by the quenching method. The conditions during the heating period were 1200°C, 1 atm. total pressure, and various partial pressures of oxygen in the range between 10^{-17} atm. and 1 atm. At the limits of this range, the stable assemblages are: (a) $f_{O_2} = 10^{-17}$ atm., MnO - $Mn_6Ta_2O_{11}$ - $Mn_4Ta_2O_9$ - $Mn_{1.4}TaO_{3.9}$ - $MnTa_2O_6$ - β-Ta_2O_5; (b) $P_{O_2} = 1$ atm., Mn_3O_4 - $Mn_{1.4}TaO_{4.2}$ - $MnTa_2O_6$ - β-Ta_2O_5. There are five univariant assemblages of three solid phases plus vapor in the phase diagram.

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INTRODUCTION

This paper follows the similar and related studies of Fe-Ta oxides[1] and Fe-Nb oxides[2]. Interest in these oxides is the result of attempts to explain the chemical relationships between tantalate and niobate minerals, especially wodginite[3, 4].

EXPERIMENTAL PROCEDURE

Reagent grade chemicals ($MnC_2O_4 \cdot 2H_2O$, precipitated from manganous sulfate and ammonium oxalate solutions, and Fansteel Ta_2O_5) were mixed to give desired proportions of Mn and Ta. Various oxygen contents in the solids were produced by variation of the oxygen partial pressure in the atmosphere within the furnace during firing. The methods of firing, oxygen pressure control, quenching, and examination of the products have been reported previously[1].

PHASE RELATIONSHIPS

The reactions of the solid phases at 1200°C and various partial pressures of oxygen, as determined by the examination of quenched products, are listed in Table 1*. There was no indication melting. Reaction rates appeared to be fast enough to reach equilibrium among the solids and vapor within the times listed in Table 1. These times vary

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*Table I has been deposited as Document No. ___ with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C.

according to the type of gas mixture in the furnace atmosphere, but the following general statement can be made: reactions go to completion within 12 hours, except in those gases rich in CO_2, i.e., CO_2:CO > 100:1, wherein complete reaction times are about 40 hours.

The Mn-Ta oxides described below have stability ranges that are limited by oxidation-reduction reactions, which, being univariant, have a fixed value of f_{O_2} (oxygen fugacity) at the fixed temperature. The data in Table I establish the stable assemblages of solid phases at six different partial pressures of oxygen in the range between $f_{O_2} = 10^{-17}$ atm. and $P_{O_2} = 1$ atm. Those phases that are stable at $f_{O_2} = 10^{-17}$ atm. are MnO-$Mn_6Ta_2O_{11}$ - $Mn_{1.4}TaO_{3.9}$ - $MnTa_2O_6$ - β-Ta_2O_5. Those phases that are stable at $P_{O_2} = 1$ atm. are Mn_3O_4 - $Mn_{1.4}TaO_{4.2}$ - $MnTa_2O_6$ - Ta_2O_5. Each group defines an isothermal, isobaric (considering f_{O_2} as the pressure variable) tie-line. These tie-lines have been projected on to one composition triangle to form the phase diagram (Figure 1). The value of f_{O_2} for each of the univariant reactions, which are represented by numbered compatability triangles in Figure 1, and which are listed in Table II, were bracketed between f_{O_2} values of the determined tie-lines.

The tie-lines H-Q (Mn_3O_4 - $Mn_6Ta_2O_{11}$) and S-M ($Mn_4Ta_2O_9$ - $Mn_{1.4}TaO_{4.2}$) are shown dashed in Figure 1, because they were not positively established. It is possible that the tie-line L-H ($Mn_{1.4}TaO_{3.9}$ - Mn_3O_4) could be stable instead of the tie-line S-M.

Compounds of Mn (III) and Mn (IV) may be expected to be stable at higher oxygen pressures and/or lower temperatures than those used in this investigation. Similarly, those phases on the join MnO-Ta_2O_5 may be expected to coexist with a metal phase at lower oxygen pressures and/or higher temperatures.

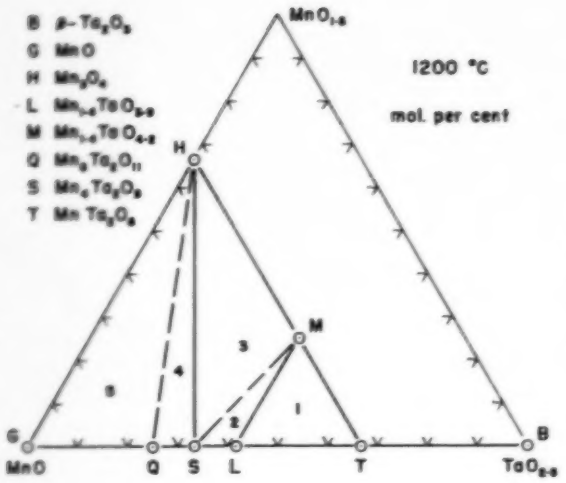

Figure 1
An isothermal, polybaric projection of a portion of the system Mn-Ta-O, showing compounds that are stable in the range of oxygen pressures 10^{-17} to 1 atm. The 3-solid-phase triangles are numbered (see Table II for list of univariant conditions).

DESCRIPTION OF THE COMPOUNDS

1. MnO, designated "G" in tables and figures

A range of non-stoichiometry of 50.0 to 51.0 at.% oxygen at 1500°C has been reported[5] for this oxide. In this investigation, bright green crystals of presumably stoichiometric material were produced at log f_{O_2} = -17 and at log f_{O_2} = -12. At conditions of log f_{O_2} = -7, which is slightly below the oxidation limit, the green MnO changed to dull greenish black, but the weight gain corresponded only to the correction for the crucible. The range of non-stoichiometry at 1200°C is, therefore, less than 0.2 at.% oxygen, which is the limit of uncertainty of these experiments.

No ternary solid solution was detected.

The oxidation of MnO to Mn_3O_4 is reported to have an equilibrium at log P_{O_2} = -4.4 at 1200°C[6]. This value of P_{O_2} is in agreement with the

value, log $f_{O_2} = -5.4 \pm 1.6$, that is assigned in the present work to this reaction and the assemblage 5 of Figure 1 and Table 2. Table 1 shows that the assemblage (MnO + $Mn_6Ta_2O_{11}$) was found at log $f_{O_2} = -7.0$, and the assemblage (Mn_3O_4 + $Mn_4Ta_2O_9$) at log $f_{O_2} = -3.8$.

2. Mn_3O_4, designated "H"

This brown oxide is known to have a rapid structural transition at 1160°C[7]. The high-temperature, cubic form cannot be preserved by quenching[7], and, in this study of quenched materials, only the low-temperature, tetragonal form was found.

No ternary solid solution was found for Mn_3O_4.

The oxidation of Mn_3O_4 to Mn_2O_3 is variously reported to have an equilibrium P_{O_2} value of $10^{1.2}$ atm.[6] or of $10.^{0.6}$ atm.[8] at 1200°C, both of which are greater than the maximum (1 atm.) used in this study.

3. $Mn_6Ta_2O_{11}$, designated "Q"

This pale-brown oxide is characterized by the X-ray powder diffraction pattern given in Table III. Its upper stability limit at 1200°C is that of the univariant reaction assemblage 4 in Figure 1 and Table II.

4. $Mn_4Ta_2O_9$, designated "S"

The synthesis of this pale-pink oxide, with a hematite-type structure and cell dimensions $\underline{a} = 5.337$ A, $\underline{c} = 14.333$ A, has been previously reported[9]. Its upper stability limit at 1200°C with variable oxygen pressure is that of the univariant assemblage 3 in Figure 1 and Table II.

5. $Mn_{1.4}TaO_{3.9}$, designated "L"

This pale-brown oxide is characterized by the X-ray powder pattern listed in Table III. Its composition was found to be bracketed by the Mn:Ta atomic ratios of 3:2 and 4:3. It may be oxidized by the reaction:

$$Mn_{1.4}TaO_{3.9} + 0.15O_2 \rightleftharpoons Mn_{1.4}TaO_{4.2}$$

which has the univariant conditions $\log f_{O_2} = -1.6 \pm 1.0$ at 1200°C. This reaction also forms the two univariant 3-solid-phase assemblages 1 and 2 in Figure 1 and Table II. This phase is not stable at temperatures lower than 1160 ± 15°C.

6. $Mn_{1.4}TaO_{4.2}$, designated "M"

This black oxide was found to have a similar Mn:Ta ratio to that of phase L, and to be related to it by the above oxidation-reduction reaction (see paragraph 5). The two phases have a similar strongest reflection in their X-ray powder diffraction patterns (see Table III).

7. $MnTaO_4$, designated "P"

This compound of Mn(III) is not stable at 1200°C under the oxygen pressures studied in this work but it was synthesized at temperatures lower than 1000°C at 1 atm. oxygen pressure and used as a starting material (see Table I). It is, therefore, expected that it would appear on the 1200°C phase diagram if a higher range of oxygen pressures were investigated.

8. $MnTa_2O_6$, designated "T"

This pinkish-white oxide is an end-member of the orthorhombic columbite mineral series. Its cell dimensions have already been reported[4]. It is stable at 1200°C across the whole range of oxygen pressures studied here. It is expected that it would oxidize at slightly higher oxygen pressures in a manner analogous to that described for $FeTa_2O_6$[1].

9. β-Ta_2O_5, designated "B"

This oxide is stable across the whole range of oxygen pressures studied here. The incorporation of a small amount of Mn(III) into material heated at 1200°C, P_{O_2} = 1 atm., is indicated by the development of a bright-yellow color. The amount of Mn in solid solution, estimated from amounts of coexisting phases, is less than 0.3 at.% Mn.

Ternary solid solutions with up to about 8 at.% of Mn(III) may be produced at lower temperatures, by firing the poorly-crystallized starting chemicals together in air at 880°C. The X-ray powder pattern of this material indicates that it is hexagonal, with $\underline{a}$ = 3.61, $\underline{c}$ = 3.85 A. It appears that the manganese substitution can stabilize the hexagonal structure that is distorted to orthorhombic in β-Ta_2O_5[10]. This phase, which is referred to as β'-Ta_2O_5 in Table 1, is not stable at temperatures higher than 1000°C.

ACKNOWLEDGEMENTS

The author wishes to thank N. F. H. Bright, Head, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, who organized this project, and A. H. Webster for helpful suggestions. Technical help was received from various members of the staff of the Mineral Sciences Division.

TABLE I

Reactions Observed at T = 1200°C and Various Oxygen Pressures

The reactions, as listed, show only the solid phases involved, vapor not being listed. In order to balance these equations, O_2 must be added where appropriate. In any assemblage, the phases are listed in order of abundance. Abbreviations: f_{O_2} = oxygen pressure (calculated value), B = β-Ta_2O_5, B′ = β'-Ta_2O_5, G = MnO, H = Mn_3O_4, L = $Mn_{1.4}TaO_{3.9}$, M = $Mn_{1.4}TaO_{4.2}$, P = $MnTaO_4$, Q = $Mn_6Ta_2O_{11}$, S = $Mn_4Ta_2O_9$, T = $MnTa_2O_6$.

f_{O_2} (atm) Gas Mixture	Mn:Ta (atomic ratio)	Time (hours)	Reaction (only solids noted)	Change in at.% oxygen in solids
10^{-17}	1:24	7	B + T ⟶ B + T	71.1 ⟶ 70.9
	1:2	24	T ⟶ T	66.7 ⟶ 66.7
	2:3	20	T + S ⟶ T + L	65.5 ⟶ 65.5
	1:1	120	L + T ⟶ L + T	63.6 ⟶ 63.6
CO	5:4	23	T + H ⟶ L + T	64.4 ⟶ 62.5
	4:3	88	S + T ⟶ L + T	- -
	5:3	69	S + T + L ⟶ S + L + T	61.0 ⟶ 61.0
	2.7:1	25	T + H ⟶ Q + S	61.9 ⟶ 58.4
	7:2	24	S + G ⟶ Q + G	57.2 ⟶ 57.2
	24:1	68	G + Q ⟶ G + Q	51.5 ⟶ 51.5
	1:0	18	G ⟶ G	50.0 ⟶ 50.0

Table I continued on next page.

TABLE I (continued)

f_{O_2} (atm) Gas Mixture	Mn:Ta (atomic ratio)	Time (hours)	Reaction (only solids noted)	Change in at.% oxygen in solids
$10^{-11.8}$	1:24	4	B + T ⟶ B + T	70.9 ⟶ 70.9
	1:9	8	B′ ⟶ B + T	71.4 ⟶ 70.1
	1:9	5	B + T ⟶ B + T	70.4 ⟶ 70.1
	1:2	4	T ⟶ T	66.7 ⟶ 66.7
	1:1	4	P ⟶ L + T	66.7 ⟶ 63.6
$\frac{CO}{CO_2} = 3$	1:1	5	M + T ⟶ L + T	64.6 ⟶ 63.6
	1:1	15	L + T ⟶ L + T	63.6 ⟶ 63.6
	4:3	5	S + T ⟶ L + T + S	62.2 ⟶ 62.2
	3:2	4	S + T ⟶ S + L + T	61.5 ⟶ 61.5
	3:2	12	S + T ⟶ S + L	61.5 ⟶ 61.5
	5:3	23	S + T ⟶ S + T + L	61.0 ⟶ 61.0
	2:1	4	S ⟶ S	60.0 ⟶ 60.0
	3:1	3	S + G ⟶ Q	57.9 ⟶ 57.9
	3:1	3	M + H ⟶ Q	61.5 ⟶ 57.9
	7:1	3	S + G ⟶ Q + G	- -
$10^{-9.0}$	1:1	7	P ⟶ L + T	66.7 ⟶ 64.6
	4:3	6	S + T ⟶ L	62.2 ⟶ 62.2
$\frac{CO}{CO_2} = \frac{1}{10}$	3:2	4	S + T ⟶ L + S + T	61.5 ⟶ 61.5
	7:3	8	S ⟶ S + Q	59.7 ⟶ 59.2
	3:1	4	S + H ⟶ Q	- -
	7:1	4	S + G ⟶ Q + G	- -
$10^{-7.0}$				
$\frac{CO}{CO_2} = \frac{1}{100}$	7:3	268	S + Q ⟶ S + Q	59.2 ⟶ 59.2
	7:1	165	S + H ⟶ Q + G	58.2 ⟶ 54.3
	24:1	48	G + Q ⟶ G + Q	51.6 ⟶ 51.5
	1:0	54	G G	50.0 ⟶ 50.0
$10^{-3.8}$				
CO_2 (purified)	7:2	22	S + G ⟶ S + H	57.2 ⟶ 59.1
	24:1	41	G + Q ⟶ H + S	51.7 ⟶ 57.6

Table I continued on next page.

TABLE I (continued)

f_{O_2} (atm) Gas Mixture	Mn:Ta (atomic ratio)	Time (hours)	Reaction (only solids noted)	Change in at.% oxygen in solids
$10^{-2.5}$	1:1	11	P ⟶ L + T	- ⟶ -
	5:4	88	T + H + M ⟶ L + T	64.4 ⟶ 62.5
	4:3	7	S + T ⟶ L + T	62.2 ⟶ 62.2
CO_2	4:3	8	M ⟶ L + M	63.8 ⟶ 62.4
(tank)	3:2	47	L + S + M ⟶ L + S	62.1 ⟶ 62.0
	5:3	67	S + M + L ⟶ S + L	61.1 ⟶ 61.0
	2:1	4	S ⟶ S	60.0 ⟶ 60.0
	2:1	11	M + H ⟶ S	62.1 ⟶ 60.1
	7:3	9	S + G ⟶ S + H	59.7 ⟶ 60.0
	2.7:1	64	T + H + P ⟶ S + H	61.9 ⟶ 59.6
	3:1	8	S + G + Q ⟶ S + H	57.9 ⟶ 59.1
	7:1	15	Q + G ⟶ S + H	54.3 ⟶ 58.2
$10^{-0.68}$	2:3	24	T + S ⟶ T + M	65.5 ⟶ 66.0
	1:1	4	P ⟶ M + T	- ⟶ -
Air	5:4	43	P + H + M ⟶ M + T	64.4 ⟶ 64.0
	4:3	7	L ⟶ M	62.2 ⟶ 63.6
	3:2	7	S + T ⟶ M	61.6 ⟶ 63.1
	5:3	17	S + T ⟶ M + H	61.0 ⟶ 62.6
	2:1	4	S ⟶ M + H	- ⟶ -
	2:1	15	M + H ⟶ M + H	62.5 ⟶ 62.1
	7:3	15	S + Q ⟶ M + H	59.2 ⟶ 61.6
	3:1	4	S + G ⟶ M + H	57.9 ⟶ 61.2
	7:1	4	S + G ⟶ H + M	54.3 ⟶ 59.3
	24:1	19	G + Q ⟶ H + M	51.5 ⟶ 57.9
P_{O_2} = 1 atm	1:24	43	B + T ⟶ B + T	70.9 ⟶ 70.9
	1:9	8	B′ ⟶ B + T	71.1 ⟶ 70.4
	1:2	5	T ⟶ T	66.7 ⟶ 66.7
	1:1	4	P ⟶ T + M	- ⟶ -
Oxygen	4:3	18	L + T ⟶ M + T	62.2 ⟶ 63.9
	3:2	88	L + S ⟶ M + H	62.0 ⟶ 63.4
	2:1	4	S ⟶ M + H	60.0 ⟶ 62.5
	3:1	14	M + H ⟶ M + H	61.2 ⟶ 61.2
	7:2	22	S + G ⟶ M + H	57.2 ⟶ 60.8
	7:1	4	S + G ⟶ M + H	54.3 ⟶ 59.3

TABLE II

Univariant Assemblages from Figure 1

Assemblage	log f_{O_2} at 1200°C
1. T + M + L + V (vapor)	-1.6 ± 1.0
2. S + M + L + V	-1.6 ± 1.0
3. S + M + H + V	-1.6 ± 1.0
4. S + H + Q + V	-5.4 ± 1.6
5. H + G + Q + V	-5.4 ± 1.6

TABLE III

X-ray Powder Diffraction Patterns of Manganese-Tantalum Oxides

$Mn_6Ta_2O_{11}$		$Mn_{1.4}TaO_{3.9}$		$Mn_{1.4}TaO_{4.2}$	
Int.	d (A)	Int.	d (A)	Int.	d (A)
2	5.61	5	7.29	2	7.03
45	4.45	40	4.44	3	5.95
6	4.21	10	4.13	3	5.64
45	4.05	5	3.95	7	3.51
2	3.12	15	3.49	15	3.47
		8	3.12	6	3.29
90	2.73	100	2.87	7	3.24
100	2.67	10	2.72	5	3.20
15	2.41	2	2.62	100	2.86
10	2.34	30	2.50	50	2.79
10	2.30	15	2.44	4	2.54
10	2.26	2	2.25	40	2.48
5	2.23	1	2.23	5	1.985
6	2.21	15	2.19	3	1.969
35	1.914	5	2.09	4	1.814
40	1.797	4	2.08	15	1.800
5	1.746	2	2.04	12	1.794
5	1.740	5	2.01	8	1.781
5	1.719	15	1.848	35	1.762
10	1.594	5	1.822	30	1.731
35	1.558	10	1.817	5	1.713
20	1.547	20	1.778	7	1.623
6	1.492	35	1.752	7	1.583
6	1.371	10	1.734	10	1.506
10	1.352	10	1.731	15	1.501
10	1.341	1	1.650	20	1.493
		2	1.608	10	1.473
		1	1.588	8	1.439
		3	1.526	8	1.435
		30	1.512		
		15	1.482		
		10	1.478		
		5	1.439		

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